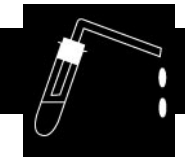
Mersmann A (1988) Design of crystallisers. *Chemical Engineering Process* 23: 213–228.
Mersmann A (1995) *Crystallisation Technology Handbook*. New York: Marcel Dekker.
Meyerson AS (1993) *Handbook of Industrial Crystallisation*. Boston: Butterworth Heinemann.
Mullin JW (1993) *Crystallisation*. Boston: Butterworth Heinemann.
Mumtaz HS, Hounslow, MJ, Seaton NA and Paterson WR (1997) Orthokinetic aggregation during precipitation: a computational model for calcium oxalate. *Transactions of the IChemE* 75: 152–159.
Mutaftschiev B (1993) Nucleation theory. In: Hurle DTJ (ed.) *Handbook of Crystal Growth*, vol. 1A, pp. 187–247. Amsterdam: Elsevier.
Nicmanis M and Hounslow MJ (1998) Finite-element methods for steady-state population balance equations. *AIChE Journal* 44: 2258–2272.
Nyvlt J (1992) *Design of Crystallisers*. Boca Raton, FL: CRC Press.
Ó Meadhra R, Kramer HJM and van Rosmalen GM (1996) A model for secondary nucleation in a suspension crystalliser. *AIChE Journal* 42: 973–982.
Ottens EPK, Janse AH and De Jong EJ (1972) Secondary nucleation in a stirred vessel cooling crystalliser. *Journal of Crystal Growth* 13/14: 500–505.
Ploß R, Tengler T and Mersmann A (1989) A new model of the effect of stirring intensity on the rate of secondary nucleation. *Chemical Engineering Technology* 12: 137–146.
Randolph AD and Larson MA (1988) *Theory of Particulate Processes*. 2nd edn. New York: Academic Press.
Sinnott RK (1998) In: *Chemical Engineering Design*, vol. 6. (Coulson JM and Richardson JF eds.), Oxford: Butterworth Heinemann.
Söhnel O and Garside J (1992) *Precipitation*. Oxford: Butterworth Heinemann.
van der Eerden JP (1993) Crystal growth mechanisms: In: Hurle DTJ (ed.) *Handbook of Crystal Growth*, vol. 1A, pp. 307–477. Amsterdam: Elsevier Science.
van der Heijden AEDM, van der Eerden JP and van Rosmalen GM (1994) The secondary nucleation rate; a physical model. *Chemical Engineering Science* 3103–3113.
Volmer M (1939) *Kinetik der Phasenbildung*. Dresden: Steinkopf.

DISTILLATION



DropBooks

R. Smith and M. Jobson, Department of Process Integration, UMIST, Manchester, UK

Copyright © 2000 Academic Press

Introduction

Distillation is the most commonly used method for the separation of homogeneous fluid mixtures. Separation exploits differences in boiling point, or volatility, between the components in the mixture. Repeated vaporization and condensation of the mixture allows virtually complete separation of most homogeneous fluid mixtures. The vaporization requires the input of energy. This is the principal disadvantage of distillation: its high energy usage. However, distillation has three principle advantages over alternative methods for the separation of homogeneous fluid mixtures:

1. The ability to handle a wide range of feed flow rates. Many of the alternative processes for the separation of fluid mixtures can only handle low flow rates, whereas distillation can be designed for the separation of extremely high or extremely low flow rates.
2. The ability to separate feeds with a wide range of feed concentrations. Many of the alternatives to distillation can only separate feeds that are already relatively pure.
3. The ability to produce high product purity. Many of the alternatives to distillation only carry out a partial separation and cannot produce pure products.

It is no accident that distillation is the most common method for the separation of homogeneous mixtures. It is a versatile, robust and well-understood technique. We shall start explaining distillation by a single-stage separation, before understanding how to set up a cascade of separation stages, which is distillation.

Single-Stage Separation

Consider the liquid mixture illustrated in **Figure 1**. If this liquid mixture is partially vaporized then the vapour becomes richer in the more volatile components (i.e. those with the lower boiling points) than the liquid phase. The liquid becomes richer in the less volatile components (i.e. those with the higher boiling points). If we allow the system in Figure 1 to come to equilibrium conditions, then the distribution of the components between the vapour and liquid phases is

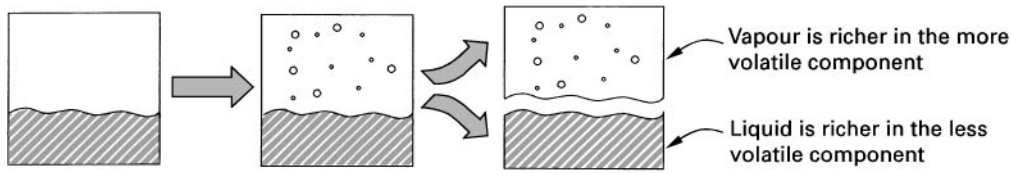


Figure 1 Partial vaporization of a liquid mixture creates a separation.

dictated by thermodynamic vapour–liquid equilibrium considerations. All components can appear in both phases. However, involatile components will tend to stay in the liquid phase.

Rather than partially vaporize a liquid, as shown in Figure 1, we could have started with a mixture of components in the vapour phase and partially condensed the vapour. We would still have had a separation, as the liquid which was formed would be richer in the less volatile components, while the vapour would have become depleted in the less volatile components. Again, the distribution of components between the vapour and liquid is dictated by thermodynamic vapour–liquid equilibrium considerations if we allow the system to come to equilibrium. Any noncondensable components present in the vapour will tend to stay in the vapour phase.

For each component in the mixture, thermodynamic equilibrium is given by the condition when the vapour and liquid fugacities are equal:

$$f_i^v = f_i^L \quad [1]$$

Fugacity is a thermodynamic pressure which, when substituted for pressure in thermodynamic expressions for ideal systems, allows them to be used for nonideal systems. It can be thought of as an escaping tendency. Defining the vapour phase fugacity coefficient ϕ_i^v:

$$f_i^v = y_i \phi_i^v P \quad [2]$$

Defining the liquid-phase fugacity coefficient ϕ_i^L and activity coefficient γ_i:

$$f_i^L = x_i \phi_i^L P \quad [3]$$

or:

$$f_i^L = x_i \gamma_i f_i^0 \quad [4]$$

For moderate pressures f_i^0 is usually taken to be the saturated vapour pressure P_i^{SAT}:

$$f_i^L = x_i \gamma_i P_i^{SAT} \quad [5]$$

These equations can be combined to give an expression for the constant, K:

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^v} \quad [6]$$

This expression provides the basis for vapour–liquid equilibrium calculations based on equations of state (e.g. Peng–Robinson equation). Alternatively:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^{SAT}}{\phi_i^v P} \quad [7]$$

This expression provides the basis for vapour–liquid equilibrium calculations based on liquid-phase activity coefficient models (e.g. Wilson equation). At moderate pressures:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^{SAT}}{P} \quad [8]$$

When the liquid phase behaves as an ideal solution, this expression simplifies to:

$$K_i = \frac{y_i}{x_i} = \frac{P_i^{SAT}}{P} \quad [9]$$

which is Raoult's law. Correlations are available to relate component vapour pressure to temperature (e.g. the Antoine equation), activity coefficients to composition and temperature (e.g. the Wilson equation) and fugacity coefficient to mixture, pressure and temperature (e.g. from the Peng–Robinson equation of state). Regression analysis of experimental data provides the adjustable parameters used in the various models.

The ratio of equilibrium constants for two components measures their relative volatility:

$$\alpha_{ij} = \frac{K_i}{K_j} \quad [10]$$

where α_{ij} is the relative volatility between components i and j.

Figure 2 shows the vapour–liquid equilibrium behaviour for a binary mixture of benzene and toluene.

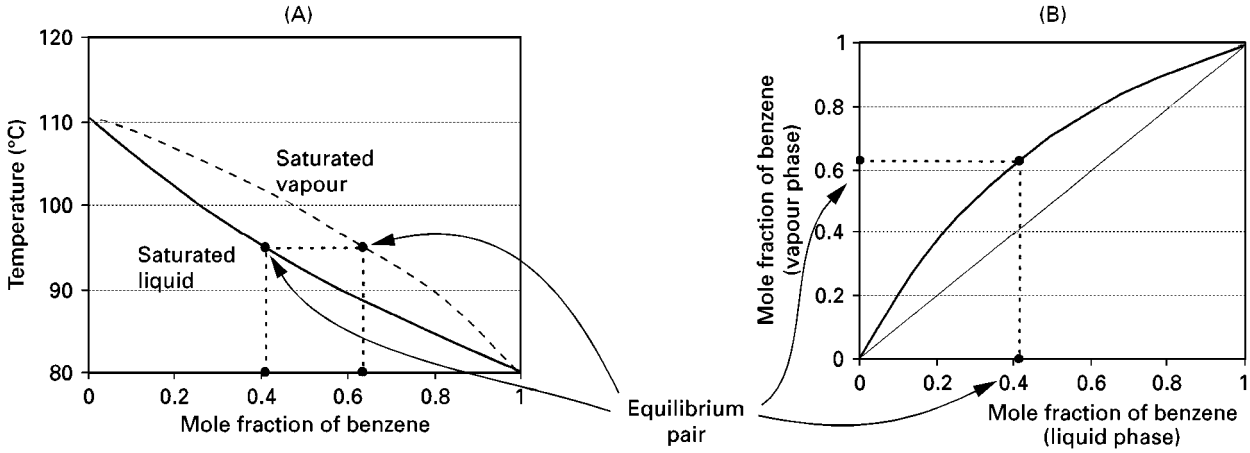


Figure 2 Vapour–liquid equilibrium for a binary mixture of benzene and toluene at a pressure of 1 atm.

Figure 2A shows the behaviour of the temperature of the saturated liquid and saturated vapour as the mole raction of benzene is varied (the balance being toluene).

Figure 2A also shows a typical vapour–liquid equilibrium pair where the mole fraction of benzene in the liquid phase is 0.4 and that in the vapour phase is 0.62. Shown in Figure 2B is an alternative way of representing the vapour–liquid equilibrium behaviour (x–y diagram). This plots the mole fraction of benzene in the vapour versus mole fraction of benzene in the liquid. A diagonal line across this diagram would represent a situation where the concentration in the vapour and the liquid are equal. The phase equilibrium behaviour, however, shows a curve above the diagonal line. This indicates that the benzene has a higher concentration in the vapour phase than the toluene, i.e. the benzene is the more volatile component in this case. Figure 2B shows the same vapour–liquid equilibrium pair as that shown in Figure 2A with a mole fraction of benzene in the liquid phase of 0.4 versus a mole faction in the vapour phase of 0.62.

Figure 3 shows a single equilibrium stage. Liquid is fed with composition x_0 and vapour is fed with composition y_2. Contact between the vapour and the liquid streams makes the vapour richer in the more volatile components and the liquid richer in the less volatile components. Once the feed conditions and compositions, the system pressure and the relative flow rates of the vapour and liquid have been fixed, then the temperature and compositions of the exit streams are unique. Let us also, initially, make a simplifying assumption that the molar flow rates of the liquid L and molar flow rates of the vapour V are constant for the stage. This assumption is known as constant molar overflow and is true if sensible heat effects are small, molar latent heats of vaporization of the components are equal, heat of mixing is negligible and there are no heat losses or gains. Let us now carry out a mass balance around the equilibrium stage shown in Figure 3. First we assume constant molar overflow:

$$L_0 = L_1 = L \qquad [11]$$

$$V_2 = V_1 = V \qquad [12]$$

A component mass balance gives:

$$Lx_{0,A} + Vy_{2,A} = Lx_{1,A} + Vy_{1,A} \qquad [13]$$

which can be rearranged to give:

$$y_{1,A} = -\frac{L}{V}x_{1,A} + \frac{Lx_{0,A} + Vy_{2,A}}{V} \qquad [14]$$

This equation can be plotted on an x–y diagram, as shown in **Figure 4**. The mass balance line is a straight line which depends on the liquid and vapour flow rates and the feed compositions of liquid and vapour. In Figure 4 the liquid and vapour feeds are not in equilibrium. Following the mass balance line until it

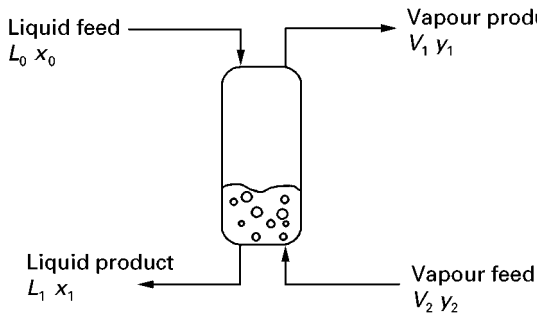


Figure 3 Separation in a single equilibrium stage.

DropBooks

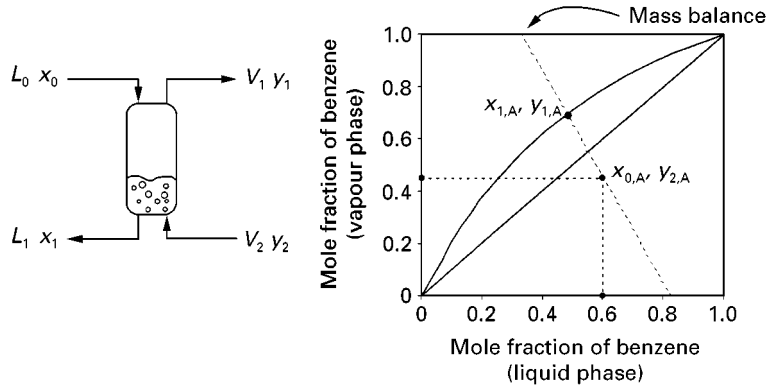


Figure 4 Single-stage separation for a binary mixture.

crosses the equilibrium line allows us to predict the vapour and liquid composition at the exit of the stage. We can now see quantitatively the separation carried out by the single equilibrium stage. However, the separation which is achieved on a single equilibrium stage is limited. We now need to consider how we can extend the idea to carry out further separation.

Cascade of Separation Stages

We have seen that a single equilibrium stage can only achieve a limited amount of separation. To extend the amount of separation we can make a cascade of stages, as shown in **Figure 5**. It is assumed in the cascade that streams leaving each stage are in equilibrium. Using a cascade of stages in this way allows the more volatile components to be transferred to the vapour phase, the less volatile components to be transferred to the liquid phase and a greater degree of separation to be achieved than for a single stage.

Figure 6 shows the liquid and vapour flows connecting the stages in a countercurrent cascade. As before, we assume constant molar overflow:

$$L_0 = L_m = \cdots = L_N; V_1 = V_m = \cdots = V_{N+1} \quad [15]$$

We can write an overall mass balance for component i across the cascade:

$$L_0 x_{0,i} + V_{N+1} y_{N+1,i} = L_N x_{N,i} + V_1 y_{1,i} \quad [16]$$

We can also write a mass balance around the envelope shown in Figure 6 over m stages:

$$L_0 x_{0,i} + V_{m+1} y_{m+1,i} = L_m x_{m,i} + V_1 y_{1,i} \quad [17]$$

This equation can be rearranged to give:

$$y_{m+1} = \frac{L}{V} \cdot x_m + \frac{V y_1 - L x_0}{V} \quad [18]$$

This operating line relates the composition streams after m stages.

Figure 7 shows the cascade in terms of a more conventional representation in a distillation column. At the top of the column we need liquid to feed the cascade. This is produced by condensing and returning some of the vapour which leaves the top stage. We also need vapour to feed the cascade at the bottom of the column. This is produced by vaporizing

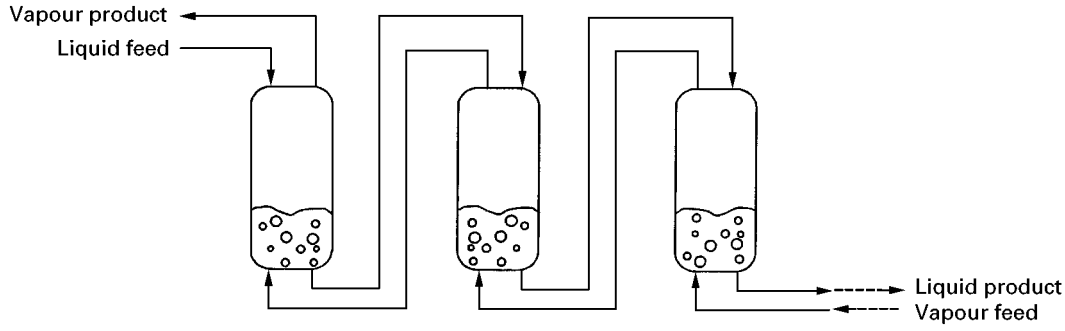


Figure 5 A cascade of separation stages.

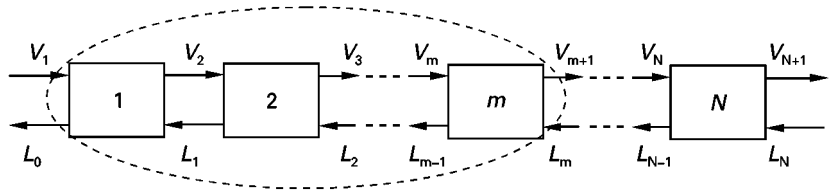


Figure 6 Mass balance on a countercurrent cascade.

and returning some of the liquid leaving the bottom stage. The feed to the process is introduced at an intermediate stage; products are removed from the condenser and the reboiler (vaporizer).

The method by which the vapour and liquid are contacted with each other in distillation columns falls into two broad categories. **Figure 8** shows a plate or tray column. Liquid enters the first tray at the top of the column and flows across what is shown in Figure 8 as a perforated plate. Liquid is prevented from weeping through the holes in the plate by the upflowing vapour. In this way the vapour and liquid are contacted. The liquid from the first tray flows over a weir and down a downcomer, to the next stage and so on. The design of stage used in Figure 8 involving a plate with simple holes is known as a sieve tray. Many other designs of tray are available involving, for example, valve arrangements for the holes in the trays. In practice, the column will need more trays than the number of equilibrium stages as mass transfer limitations prevent equilibrium being achieved on a tray.

The other broad class of contacting arrangement is that of packed columns. Here the column is filled with a solid material which has a high voidage. Liquid trickles across the surfaces of the packing and vapour flows upward through the voids in the packing, contacting the liquid on its way up the column. Many different designs of packing are available.

The design of a distillation column like the one shown in Figure 8 involves a number of steps:

1. Set the product specifications.
2. Set the operating pressure.
3. Determine the number of theoretical stages required and the energy requirements.
4. Determine the actual number of trays or height of packing needed and the column diameter.
5. Design the column internals, which involves determining the specific dimensions of the trays, packing, liquid and vapour distribution systems, etc.
6. Carry out the mechanical design to determine wall thicknesses, internal fittings, etc.

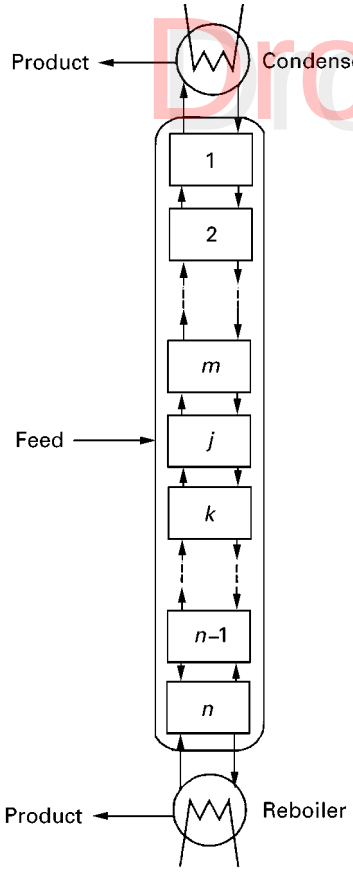


Figure 7 Refluxing and reboiling.

DropBooks

Let us start by considering the simplest case of binary distillation.

Binary Distillation

Consider the mass balance on a simple distillation column. By simple column, we mean that the column has one feed, two products, one reboiler and one condenser. Such a column is shown in **Figure 9**, together with the feed and product flow rates and compositions. We can write an overall mass balance as:

$$F = D + B \qquad [19]$$

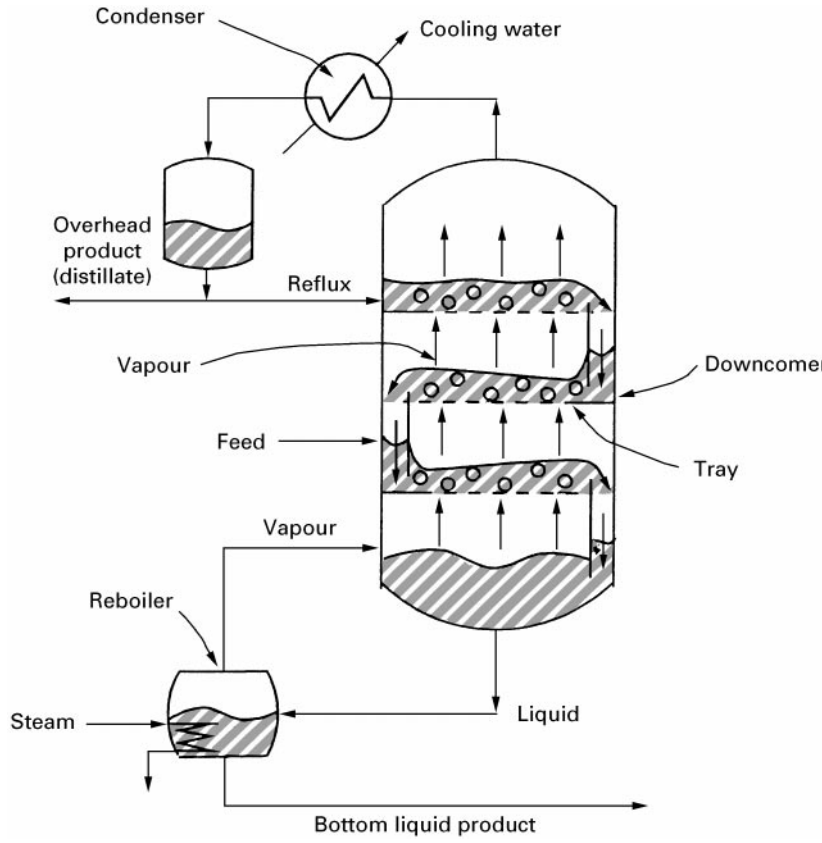


Figure 8 The distillation column.

We can also write a component balance as follows:

$$Fz_i = x_{D,i}D + x_{B,i}B \qquad [20]$$

However, to understand the design of the column more fully, we must be able to follow the mass balance throughout the column. Let us start by considering the mass balance for the part of the column above the feed – the rectifying section. **Figure 10** shows the rectifying section of a column and the flows and compositions of the liquid and vapour in the rectifying section. First we write an overall balance for the rectifying section:

$$V_{n+1} = L_n + D \qquad [21]$$

We can also write a component balance:

$$V_{n+1}y_{n+1,i} = L_n x_{n,i} + Dx_{D,i} \qquad [22]$$

We assume constant molar overflow (L and V are constant) and define the reflux ratio, R, to be:

$$R = L/D \qquad [23]$$

Given the reflux ratio, we can express the vapour flow in terms of R:

$$V = (R + 1)\,D \qquad [24]$$

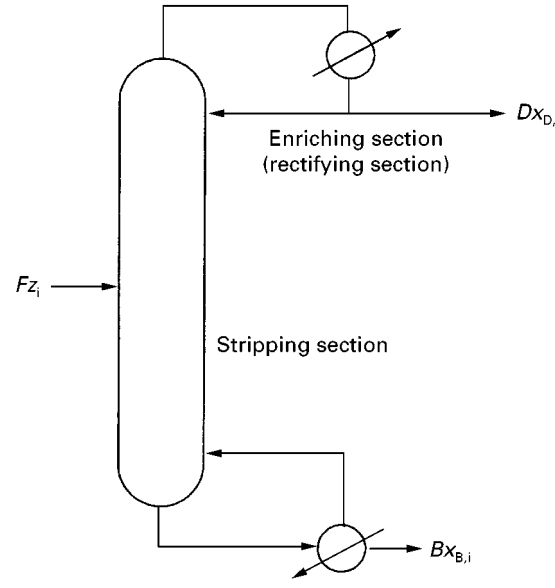


Figure 9 Mass balance on a simple distillation column.

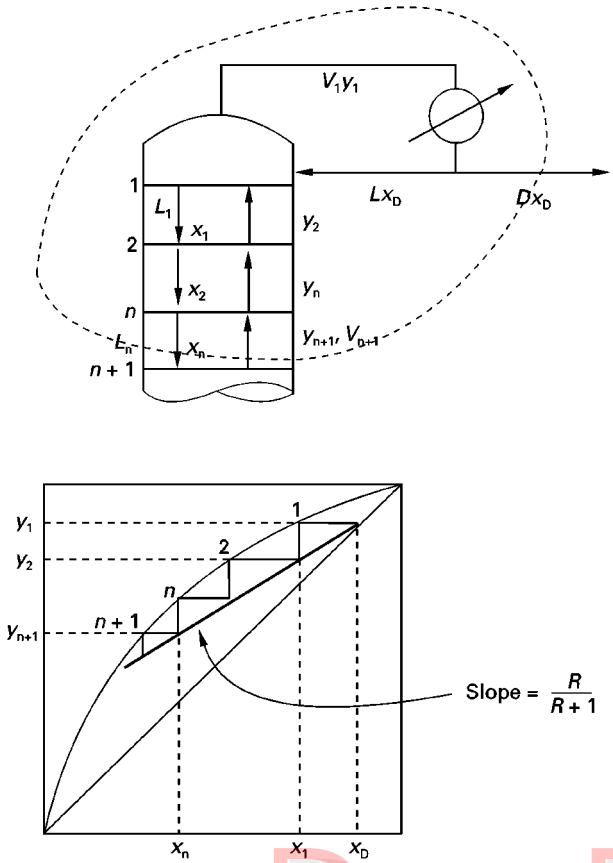


Figure 10 Mass balance on the rectifying section.

These expressions can be combined to give an equation which relates the vapour entering and liquid flows leaving stage n:

$$y_{n+1,i} = \frac{R}{R+1} x_{n,i} + \frac{1}{R+1} x_{D,i} \qquad [25]$$

On an x–y diagram for component i, this is a straight line starting at the distillate composition with slope $R/(R+1)$ and which intersects the diagonal line at $x_{D,i}$.

Starting at the distillate composition x_D in Figure 10, a horizontal line across to the equilibrium line takes us to the composition of the vapour in equilibrium with the distillate, y_1. A vertical step down takes us to the liquid composition leaving stage 1, x_1. Another horizontal line across to the equilibrium line gives us the composition of the vapour leaving stage 2, y_2. A vertical line to the operating line gives us the composition of the liquid leaving stage 2, x_2, and so on. Thus, as we step between the operating line and equilibrium line in Figure 10, we follow the change in vapour and liquid composition through the rectifying section of the column.

Now consider the corresponding mass balance for the column below the feed, the stripping section. **Figure 11**A shows the vapour and liquid flows and compositions through the stripping section of a column. An overall mass balance for the stripping section around stage m gives:

$$L_m = V_{m+1} + B \qquad [26]$$

A component balance gives:

$$L_m x_{m,i} = V_{m+1} y_{m+1,i} + B x_{B,i} \qquad [27]$$

Again, assuming constant molar overflow (L and V are constant), these expressions can be combined to give an equation relating the vapour entering and the liquid leaving stage m:

$$y_{m+1,i} = \frac{L}{V} x_{m,i} - \frac{B}{V} x_{B,i} \qquad [28]$$

We can plot this line in our x–y plot, as shown in Figure 11B. It is a straight line with slope L/V which intersects the diagonal line at x_B. Starting from the

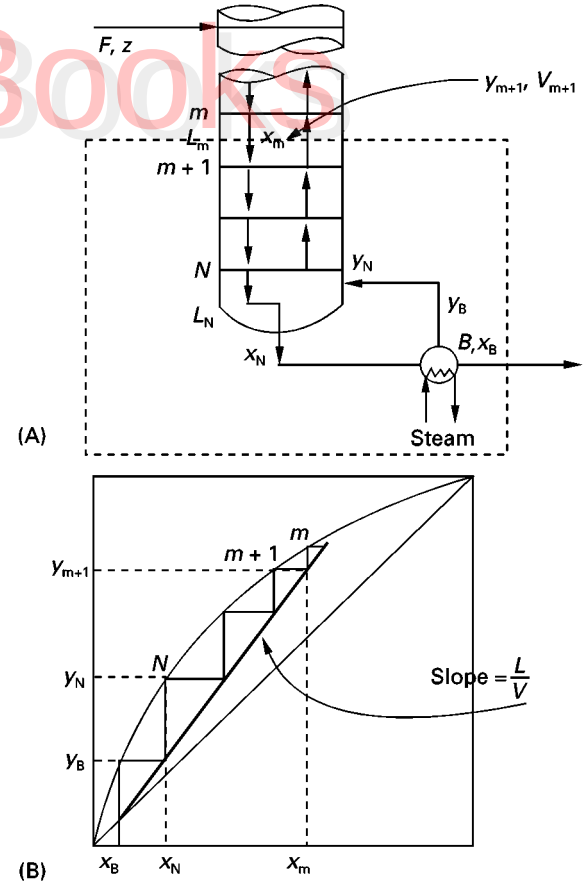


Figure 11 Mass balance on the stripping section.

DropBooks

bottom composition, x_B, a vertical line to the equilibrium line gives the composition of the vapour leaving the reboiler, y_B. A horizontal line across to the operating line gives the composition of the liquid leaving stage N, x_N. A vertical line to the equilibrium line then gives the vapour leaving stage N, y_N, and so on.

Let us now bring together the rectifying and stripping sections at the feed stage. Consider the point of intersection of the operating lines for the rectifying and stripping sections. From eqns [22] and [27]:

$$V_{n+1}y_i = L_n x_i + Dx_{D,i} \quad [29]$$

$$V_{m+1}y_i = L_m x_i - Bx_{B,i} \quad [30]$$

where y_i and x_i are the intersection of the operating lines. Subtracting eqns [29] and [30] gives:

$$(V_{n+1} - V_{m+1})y_i = (L_n - L_m)x_i + Dx_{D,i} + Bx_{B,i} \quad [31]$$

Substituting the overall mass balance, eqn [20], gives:

$$(V_{n+1} - V_{m+1})y_i = (L_n - L_m)x_i + Fz_i \quad [32]$$

Now we need to know how the vapour and liquid flow rates change at the feed stage.

What happens here depends on the condition of the feed, whether it is sub-cooled, saturated liquid, partially vaporized, saturated vapour or superheated vapour. To define the condition of the feed, we introduce the variable q, defined as:

$$q = \frac{\text{heat required to vaporize 1 mol of feed}}{\text{molar latent heat of vaporization of feed}} \quad [33]$$

For a saturated liquid feed $q = 1$ and for a saturated vapour feed $q = 0$. The flow rate of feed entering the column as liquid is $q \cdot F$. The flow rate of feed entering the column as vapour is $(1 - q) \cdot F$. **Figure 12**A shows a schematic representation of the feed stage. An overall mass balance on the feed stage for the vapour gives:

$$V_n = V_m + (1 - q)F \quad [34]$$

An overall mass balance for the liquid on the feed stage gives:

$$L_m = L_n + qF \quad [35]$$

Combining eqns [32], [34] and [35] gives a relationship between the compositions of the feed and the vapour and liquid leaving the feed tray:

$$y_i = \frac{q}{q-1} \cdot x_i - \frac{1}{q-1} \cdot z_i \quad [36]$$

This equation is known as the q-line. On the x–y plot, it is a straight line with slope $q/(q-1)$ and intersects the diagonal line at z_i. It is plotted in Figure 12B for various values of q.

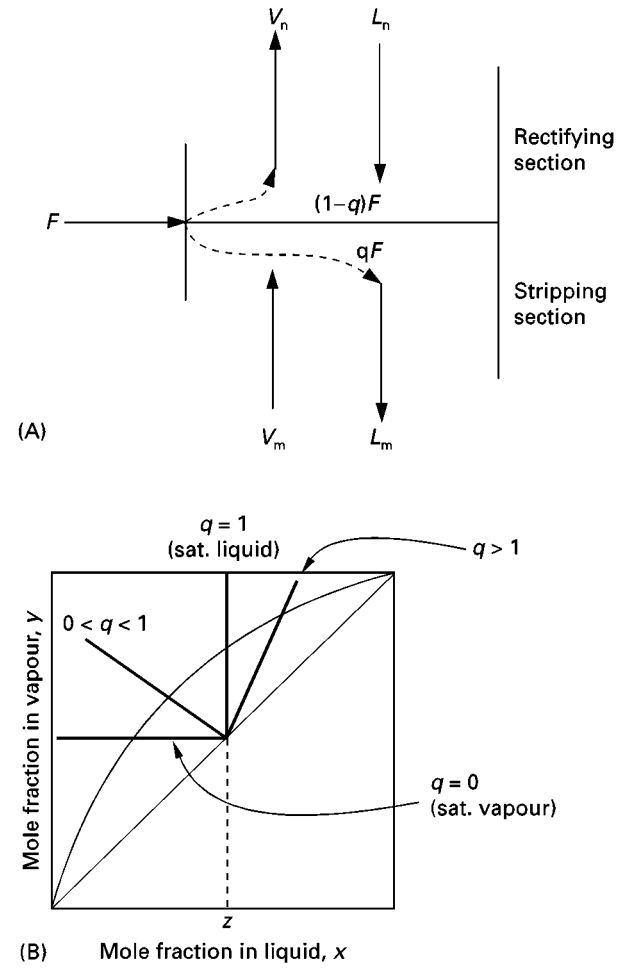


Figure 12 Mass balance for the feed stage.

We are now in a position to bring together the mass balance for the rectifying and stripping sections. **Figure 13** shows the complete design. The construction is started by plotting the operating lines for the rectifying and stripping sections. The q-line intersects the operating lines at their intersection. The intersection of the operating lines is the correct feed stage, i.e. the feed stage necessary to minimize the overall number of theoretical stages. The construction steps off between the operating lines and the equilibrium lines. The construction can be started either from the overhead composition working down or from the bottom composition working up. The

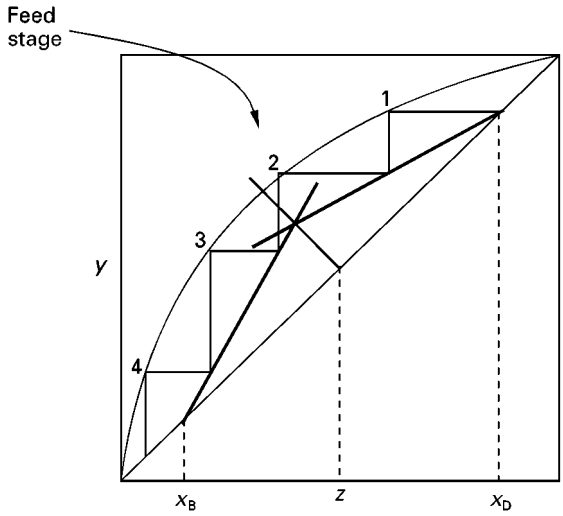


Figure 13 Combining the rectifying and stripping sections.

stepping procedure changes from one operating line to the other at the intersection with the *q*-line. We should also note that a partial reboiler represents a separation stage and a partial condenser (as opposed to a total condenser) also represents a separation stage.

There are two important limits that we need to consider for distillation. The first is illustrated in **Figure 14**A. This is total reflux in which no products are taken and there is no feed. All of the overhead vapour is refluxed and all of the bottom liquid reboiled. Figure 14A also shows total reflux on an *x*–*y* plot. This corresponds with the smallest number of stages required for the separation. The other limiting case, shown in Figure 14B, is where the reflux ratio is chosen such that the operating lines intersect at the equilibrium line. As this stepping procedure approaches the *q*-line from both ends, an infinite number of steps are required to approach the *q*-line. This is the minimum reflux condition, and we term the condition at the feed stage to be a pinch.

This method of design for binary distillation is known as the McCabe–Thiele method. It is restricted in its application because it only applies to binary systems and involves the simplifying assumption of constant molar overflow. However, it is an important method to understand as it gives important conceptual insights into distillation, which cannot be obtained in any other way.

Multicomponent Distillation

Before a multicomponent distillation column can be designed, a decision must be made as to the two key components between which it is desired to make the separation. The light key component will be the one we wish to keep out of the bottom product. The heavy key component will be the one we wish to keep out of the top product. The recovery of the light key or the concentration of the light key in the overhead

DropBooks

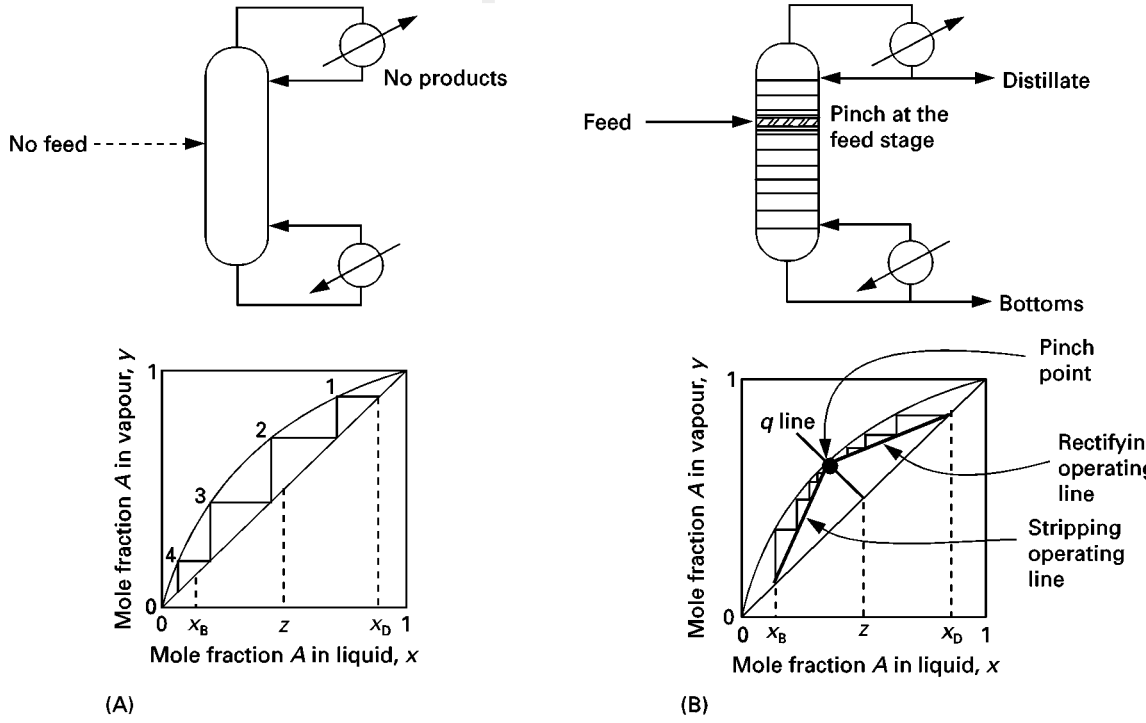


Figure 14 (A) Total and (B) minimum reflux in binary distillation.

product must be specified, as must the recovery of the heavy key or the concentration of the heavy key in the bottom product. Intermediate boiling components will distribute between the products.

A number of short-cut methods are available for the design of multicomponent distillation columns. Each considers different aspects of the design of multicomponent columns. Each of the short-cut methods involves some simplifying assumptions and the designer must be fully aware of these assumptions when applying these methods. One simplifying assumption, which all the methods have in common, is the assumption of constant relative volatility. The relative volatility for the feed composition can be calculated, but this might not be characteristic of the overall column. By making some assumption of the product compositions, the relative volatility at the top and bottom of the column can be calculated and a mean taken:

$$(\alpha_{i,j})_{mean} = \sqrt{(\alpha_{i,j})_{top} \cdot (\alpha_i^j)_{bottom}} \qquad [37]$$

Fenske Equation

The Fenske equation is used to estimate the minimum number of stages, N_{min}. This is at total reflux and the flows of component i and a reference component, r, are related by:

$$\frac{d_i}{d_r} = \alpha_{i,r}^{N_{min}} \cdot \frac{b_i}{b_r} \text{ or } \frac{x_{D,i}}{x_{D,r}} = \alpha_{i,r}^{N_{min}} \cdot \frac{x_{B,i}}{x_{B,r}} \qquad [38]$$

When component i is the light key component L, and r is the heavy key component, H, we can write:

$$N_{min} = \frac{\log\left[\frac{d_L}{d_H} \cdot \frac{b_H}{b_L}\right]}{\log \alpha_{L,H}} \qquad [39]$$

$$N_{min} = \frac{\log\left[\frac{x_{D,L}}{x_{D,H}} \cdot \frac{x_{B,H}}{x_{B,L}}\right]}{\log \alpha_{L,H}} \qquad [40]$$

$$N_{min} = \frac{\log\left[\frac{r_{D,L}}{1 - r_{D,L}} \cdot \frac{r_{B,H}}{1 - r_{B,H}}\right]}{\log \alpha_{L,H}} \qquad [41]$$

Hengstebeck–Geddes Equation

The Hengstebeck–Geddes equation is used to estimate the composition of the products. The Fenske equation can be written in the form:

$$\log\left[\frac{d_i}{b_i}\right] = A + C \log \alpha_{i,r} \qquad [42]$$

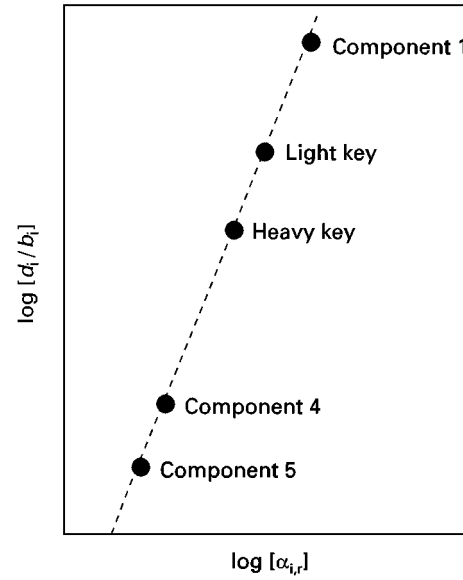


Figure 15 The Hengstebeck–Geddes method.

The parameters A and C are obtained by applying the relationship to the light and heavy key components. This allows the compositions of the non-key components to be estimated. This is illustrated in **Figure 15**. Having specified the distribution of the light and heavy key components, knowing the relative volatilities for the other components allows their compositions to be estimated. The method is based on total reflux conditions. It assumes that the component distributions do not depend on reflux ratio.

The Underwood Equations

The Underwood equations are used to estimate minimum reflux ratio. There are two equations. The first is given by:

$$\sum_{i=1}^{n} \frac{\alpha_i x_{i,F}}{\alpha_i - \theta} = 1 - q \qquad [43]$$

This equation must be solved for the root θ. This root will have a value between the relative volatilities of the light and heavy key components. Having obtained the value θ, this is then substituted into the second equation to determine the minimum reflux ratio, R_{min}:

$$R_{min} + 1 = \sum_{i=1}^{n} \frac{\alpha_i x_{i,D}}{\alpha_i - \theta} \qquad [44]$$

The Gilliland Correlation

The Gilliland correlation is an empirical relationship used to determine the number of stages, given the minimum reflux ratio R_{min} and minimum number of stages N_{min}. The original correlation was presented in

graphical form. Two parameters were used to correlate the experimental data:

$$Y = \frac{N - N_{min}}{N + 1}, \quad X = \frac{R - R_{min}}{R + 1} \qquad [45]$$

Various attempts have been made to represent the correlation algebraically. For example:

$$Y = 0.2788 - 1.3154X + 0.4114X^{0.2910} + 0.8268 \cdot \ln X + 0.9020 \ln\left(X + \frac{1}{X}\right) \qquad [46]$$

The Kirkbride Equation

The Kirkbride equation is used to estimate the most appropriate feed point for the column. It is given in the form:

$$\log \frac{N_r}{N_s} = 0.206 \log\left[\frac{z_H}{z_L} \cdot \frac{B}{D} \cdot \left(\frac{x_{B,L}}{x_{D,H}}\right)^2\right] \qquad [47]$$

Rigorous Methods

All of the above equations are approximate in some way. To develop a completely rigorous approach to distillation design, consider **Figure 16**. This shows a general stage in the distillation column. Vapour and liquid enter this stage. A liquid side-stream can be taken, as can a vapour side-stream. Feed can enter and heat can be transferred to or from the stage. This is a general stage and allows for many design options other than simple columns with one feed and two products. By using a general representation of a stage, as shown in Figure 16, designs with multiple feeds, multiple products and intermediate heat exchange are possible. We can write rigorous equations to describe the material and energy balance.

1. Material balance (N_{comp} equations for each stage):

$$L_{j-1}x_{i,j-1} + V_{j+1}y_{i,j+1} + F_j z_{i,j} - (L_j + U_j)x_{i,j} - (V_j + W_j)y_{i,j} = 0 \qquad [48]$$

2. Equilibrium relation for each component (N_{comp} equations for each stage):

$$y_{i,j} - K_{i,j}x_{i,j} = 0 \qquad [49]$$

3. Summation equations (one for each stage):

$$\sum_{i=1}^{N_{comp}} y_{i,j} - 1.0 = 0 \qquad \sum_{i=1}^{N_{comp}} x_{i,j} - 1.0 = 0 \qquad [50]$$

4. Energy balance (one for each stage):

$$L_{j-1}H^L_{j-1} + V_{j+1}H^V_{j+1} + F_j H^F - (L_j + U_j)H^L_j - (V_j + W_j)H^V_j - Q_j = 0 \qquad [51]$$

DropBooks

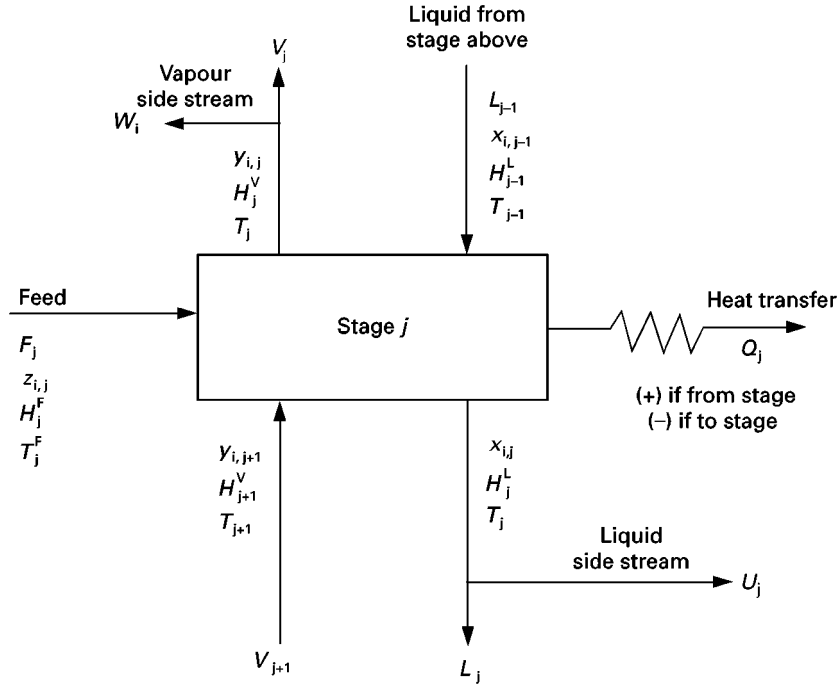


Figure 16 A general stage for rigorous methods in multicomponent distillation.

Feed	Mole fraction
Benzene	0.05
Toluene	0.15
Ethylbenzene	0.70
Styrene	0.10
Temperature	126.5 °C
Pressure	101.3 kPa
Saturated liquid	q =1
Recovery of ethylbenzene to distillate	99%
Recovery of styrene to bottom product	98%

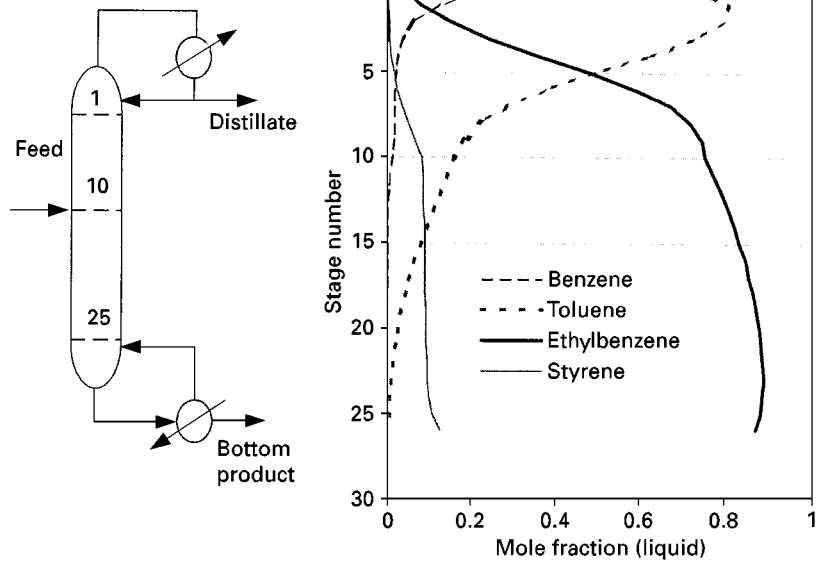


Figure 17 Simulation results for multicomponent distillation.

This set of equations must be solved iteratively and the calculations are complex. Many methods are available and in practice designers use commerical simulation packages.

Figure 17 shows a typical result for the rigorous simulation of a distillation column with a feed mixture containing benzene, toluene, ethylbenzene and styrene. Because such simulations are numerically complex and time-consuming, short-cut calculations are used to explore the various design parameters before setting up a rigorous simulation.

Choice of Operating Parameters

The feed composition and flow rate are usually fixed. Also, the product specifications are usually given in the statement of the design problem. These may be expressed in terms of product purities or recoveries of certain components. The operating parameters to be selected by the designer include:

1. operating pressure
2. reflux ratio
3. feed condition
4. feed stage location
5. type of condenser

Pressure

Once the products have been specified, the pressure must be specified before the design can proceed. Pressure has an important effect on all aspects of the distillation column design. **Figure 18** shows the trends of various properties of the distillation as

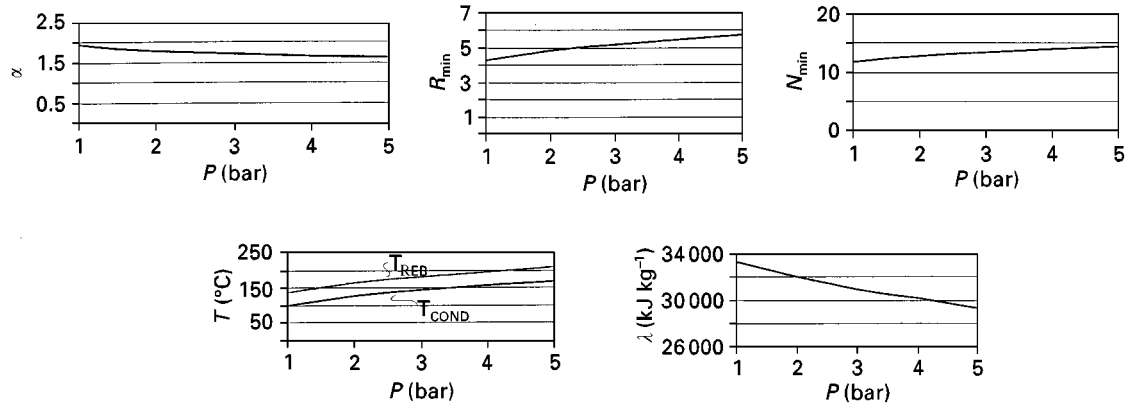


Figure 18 Effect of pressure on the distillation of a mixture of benzene, toluene, ethylbenzene and styrene.

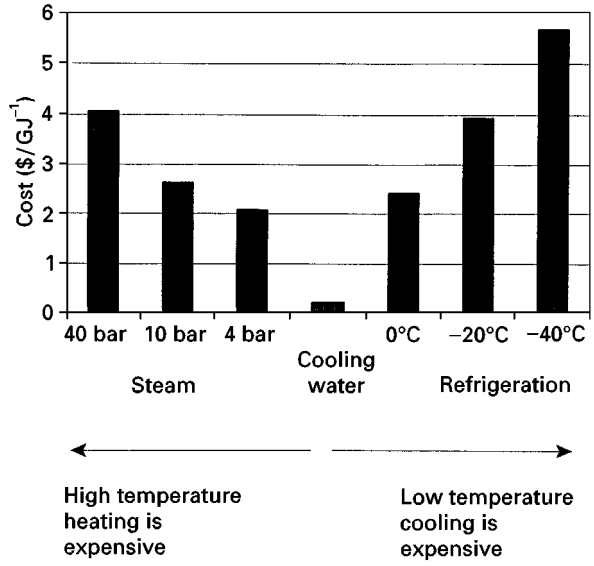


Figure 19 Effect of temperature on utility costs.

pressure increases. As pressure increases, the relative volatility decreases, making separation more difficult. Minimum reflux ratio also increases with increasing pressure, as does the minimum number of stages. All of these trends point to operating the distillation columns at a pressure as low as possible. However, the latent heat decreases with increasing pressure; this would have the effect of decreasing the reboiler duty as pressure increases. Finally, Figure 18 also shows the trend of condenser and the reboiler temperature as pressure increases; both increase with increasing pressure.

The temperature of the condenser and reboiler, as shown in Figure 18, dictate the choice of utilities to supply heating and cooling. **Figure 19** shows the trend for the variation in utility costs for heating and cooling at different temperatures. Figure 19 shows that extreme temperatures for heating and cooling require more expensive utilities. Matching the distillation condenser and reboiler against cheap utilities is usually the dominant issue when choosing the operating pressure of the distillation column.

When starting a distillation design, we usually choose to operate at atmospheric pressure unless this leads to thermal degradation of products in the reboiler because of high temperatures, or requires refrigeration in the condenser. If product degradation is a problem, then we would operate the column under vacuum conditions to decrease the temperatures of the distillation. If refrigeration is required in the condenser, then we might choose to increase the column pressure until cooling water can be used for the condenser (which means the overhead condenser temperature must be 30–40°C or higher), unless very high pressures are required for the distillation.

Choice of Reflux Ratio

Figure 20 shows the variation of the number of stages required versus the reflux ratio. Starting from minimum reflux, we require an infinite number of stages. As the reflux ratio is increased, the number of stages becomes finite and decreases towards the minimum number of stages at total reflux. Actual reflux ratios will lie somewhere between the two extremes.

Figure 21 shows a plot of annual cost versus reflux ratio. At minimum reflux ratio there is the requirement for an infinite number of stages and the annual capital cost is correspondingly infinite. However, as the reflux ratio is increased the capital cost diminishes. On the other hand, as reflux ratio is increased from the minimum, the utility costs increase steadily. Combining the annual capital costs with the annual utility costs gives a total annualized cost which shows a minimum at the optimum reflux ratio. This optimum is usually fairly flat for a significant range of reflux ratios and an initial setting of 1.1 times the minimum reflux ratio is often assumed.

Choice of Feed Condition

The feed condition affects vapour and liquid flow rates in the column, and in turn:

1. reflux ratio, heating and cooling duties
2. column diameter
3. most appropriate location of the feed stage

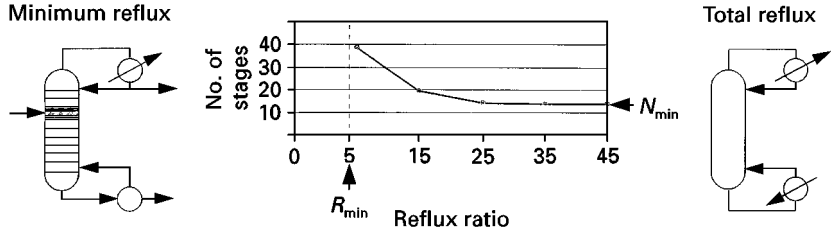


Figure 20 Range of reflux ratios.

DropBooks

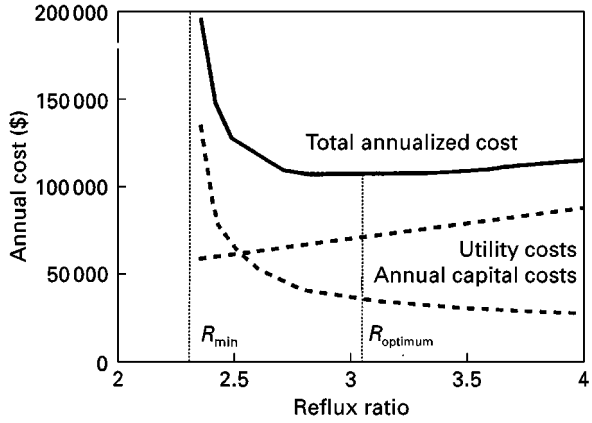


Figure 21 Capital–energy trade-offs determine the optimum reflux ratio.

The feed temperature usually lies between the extreme temperatures of the column (condenser and reboiler temperatures).

Cooling the feed:

1. decreases the number of stages in the rectifying section but increases the number of stages in the stripping section
2. requires more heat in the reboiler but decreases the cooling duty of the condenser

Heating the feed:

1. increases the number of stages in the rectifying section but decreases the number of stages in the stripping section
2. decreases the heat requirement of the reboiler but increases the cooling duty of the condenser

Heating or cooling the feed can reduce energy costs. If heat is added to the feed and saves heating in the reboiler, the heating of the feed can be carried out at a lower temperature than would be required in the reboiler. Cooling the feed can be carried out at a lower temperature than cooling in the condenser. In both cases heating or cooling the feed is done at more moderate temperatures and, in principle, with a cheaper utility.

Choice of Feed Stage Location

When choosing the feed stage location, our objective is to find a stage in the column for which the composition matches as closely as possible that of the feed. For binary distillation it is, in theory, possible to find an exact match between the composition on a stage and the composition of the feed. In practice, because there is a finite change from stage to stage, even for a binary system, an exact match may not be possible. In multicomponent systems it is highly unlikely that the composition of all of the components can be matched. Mismatches between the composition on the feed stage and that of the feed create inefficiencies in the distillation. These inefficiencies lead to an increase in the number of stages required for the same separation, or more reflux, which means increased energy requirements, or a combination of both.

Distillation Equipment

Let us now turn our attention to the equipment used for distillation operations. As pointed out previously, there are two broad classes of internals used for distillation: trays and packing.

Trays

Figure 22A shows a conventional tray arrangement. Liquid flows down a downcomer across a tray in which the upflowing vapour contacts the liquid flowing across the tray. The liquid flows down the next downcomer to the following tray, and so on. The perforated plate used in Figure 22A, known as a sieve tray, is the most common arrangement used. It is cheap, simple, and well understood in terms of its performance. There are many other designs of tray which are used. Many use simple valve arrangements in the holes to improve the performance and the flexibility of operation to be able to cope with a wider variety of liquid and vapour flow rates in the column. One particular disadvantage of the conventional tray in Figure 22A is that the downcomer arrangement makes a significant proportion of the area within the column shell not available for contacting liquid and vapour. In an attempt to overcome this, high capacity trays, with increased active area, have been developed. Figure 22B illustrates the concept. Again, many different designs are available for high capacity trays.

When designing a column to use trays, we need to know the tray efficiency to convert from

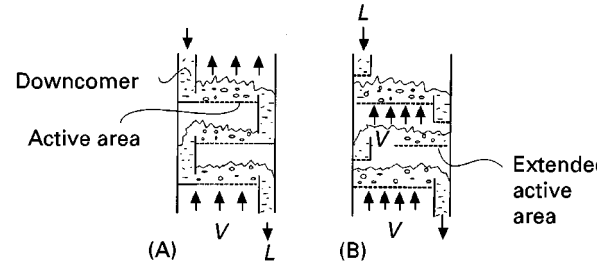


Figure 22 Distillation trays. (A) Conventional tray; (B) high capacity tray.

theoretical stages to real trays. The difference between the performance of an ideal stage and a real tray results from the fact that equilibrium is not achieved on a real tray because of mass transfer limitations. We therefore define an efficiency to convert from the theoretical stages to real trays. Three different efficiencies can be defined:

1. Overall tray efficiency, E_o:

$$E_o = \frac{\text{number of theoretical stages}}{\text{number of real stages}} \qquad [52]$$

E_o depends on the design of the tray and the mixture being distilled and typically varies between 60% and 90% for distillation.

2. Murphree tray efficiency, E_M. This characterizes the performance of individual trays rather than having an overall measure as defined by E_o. This is because efficiencies can vary throughout the column. The Murphree tray efficiency for stage j is defined as:

$$E_M = \frac{y_j - y_{j+i}}{y_j^* - y_{j+1}} \qquad [53]$$

The Murphree tray efficiency measures the change in concentration of the vapour phase for an actual tray relative to that for an ideal stage.

3. Point efficiency, E_{MP}. This measures the efficiency not only of an individual tray but at a local point on a tray. It is defined in the same way as the Murphree tray efficiency, but at a point on the tray. It is defined as:

$$E_{MP} = \frac{y_{j,local} - y_{j+1,local}}{y_{jlocal}^* - y_{j+1,local}} \qquad [54]$$

E_{MP} varies across the tray and must be integrated across the tray to obtain E_M. The result will depend on the mixing pattern on the tray. For example, if the tray is perfectly mixed then $E_M = E_{MP}$.

Correlations are available to predict E_o, E_M and E_{MP}.

Trays have a range within which they can operate satisfactorily in terms of the hydraulic design. For example, **Figure 23** shows the range of operation of a sieve tray. Using a sieve tray, internal flows in the distillation column are limited by:

1. flooding, in which liquid cannot flow down the column
2. entrainment, in which liquid drops are carried up the column by the vapour flow

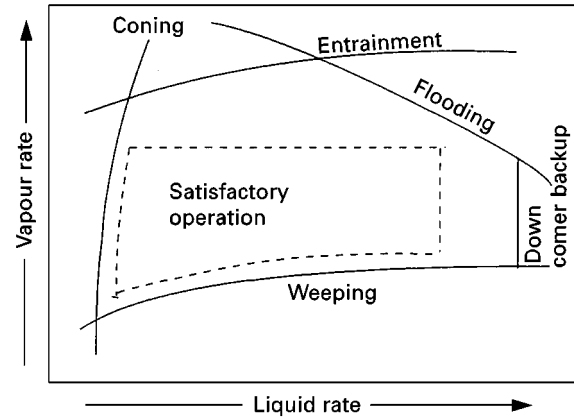


Figure 23 Sieve tray performance.

3. downcomer backup, in which liquid backs up in the downcomers
4. weeping, in which vapour flow is too low to maintain liquid on the tray
5. coning, in which poor vapour–liquid contact occurs due to the vapour forming jets

Packing

Figure 24A shows a traditional design of packing, which is random or dumped packing. The random or dumped packing is pieces of ceramic, metal or plastic which, when dumped in the column, produce a body with a high voidage. The liquid trickles down over the surfaces of the packing and the vapour is in contact with the liquid as it flows up through the voids in the packing.

Figure 24B shows structured packing. This is manufactured by sheets of metal being preformed

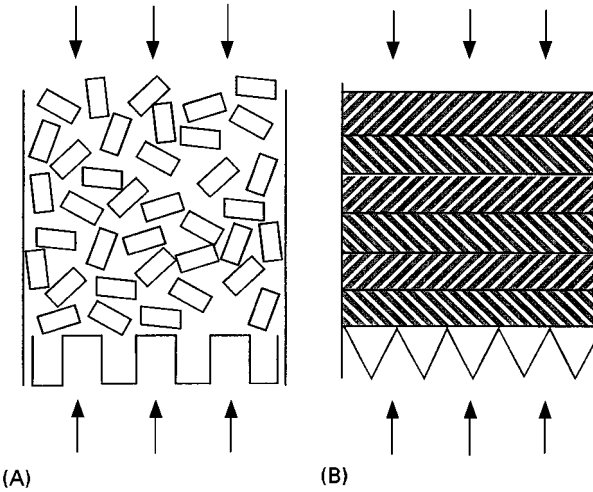


Figure 24 Distillation packing. (A) Random or dumped packing; (B) structured packing.

DropBooks

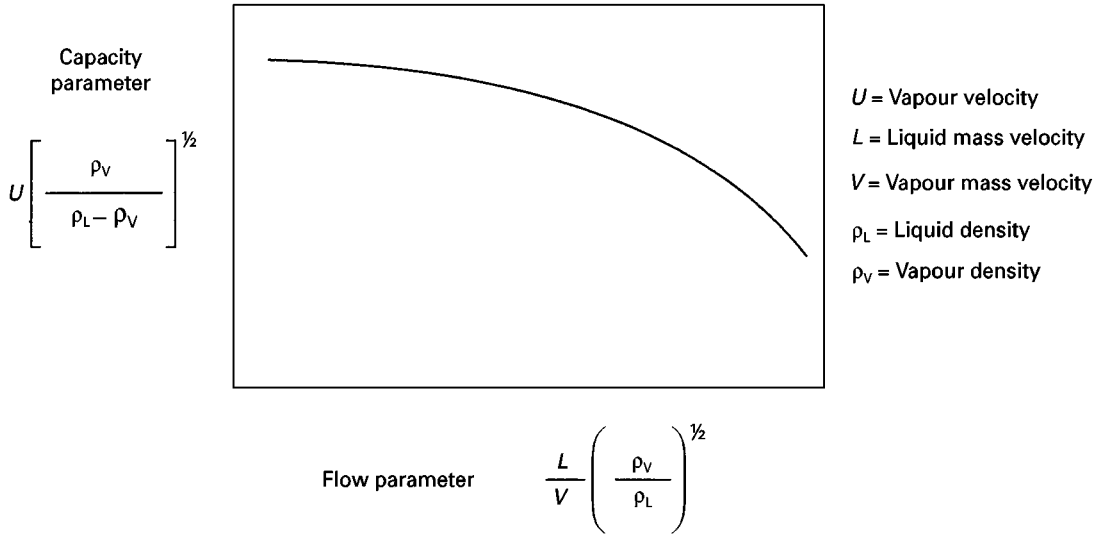


Figure 25 Flood point correlation for packing.

with corrugations and holes and then joined together to produce a preformed packing with a high voidage. This is manufactured in slabs and built up in layers within the column.

Many types of both random and structured packing are available. We need to be able to calculate the height of packing required by relating to the theoretical stages to the height of packing. For this we need the height equivalent of a theoretical plate, HETP. Thus, the packing height is simply the product of the number of theoretical stages and the HETP. Correlations are available for HETP.

As with the hydraulic design of trays, packing has a limited range over which the hydraulic design is acceptable. At very low vapour velocities through the packing, liquid flows are not influenced by the vapour flow. As the vapour velocity increases, the vapour starts to hinder the downward flow of liquid. This is the loading point. A limit is reached at a high vapour velocity, characterized by heavy entrainment of liquid and a sharp rise in the pressure drop across the packing. This is the flood point. Correlations are used to determine the flood point and a typical correlation is shown in **Figure 25**. We usually design the packing for a vapour velocity to be some proportion of the flooding velocity (e.g. 80%).

Complex Distillation Arrangements

All of the distillation arrangements which we have considered so far have involved one feed, produced two products, have a reboiler and condenser, and operation has been assumed to be continuous. Distillation designs have been adapted to suit different purposes, as discussed below.

Batch Distillation

In batch distillation, the feed is charged as a batch to the base of the distillation column. Once the feed has been charged, it is subjected to continuous vaporization. This vapour would then flow upwards through trays or packing to the condenser and reflux would be returned as with continuous distillation. However, unlike continuous distillation, the overhead product will change with time. The first material to be distilled will be the more volatile components. As the vaporization proceeds and product is withdrawn overhead, the product will become gradually richer in the less volatile components. Thus, batch distillation allows different fractions to be taken from the same feed. The batch distillation strategy depends on both the feed mixture and the products required from the distillation. By careful control of the reflux, it is possible to hold the composition of the distillate constant for a time until the required reflux ratio becomes intolerably large, as illustrated in **Figure 26**.

Azeotropic Distillation

Figure 27 shows an x–y diagram in which the equilibrium curve crosses the diagonal line. At the point where the equilibrium curve crosses the diagonal, the vapour and liquid have the same composition; this is an azeotrope. A mixture in which the vapour and liquid have the same composition cannot be separated by conventional distillation. There are two means by which a mixture such as that shown in Figure 27 can be separated. The first uses two columns operating at different pressures and takes advantage of the fact that the composition of the azeotrope might change significantly with a change in

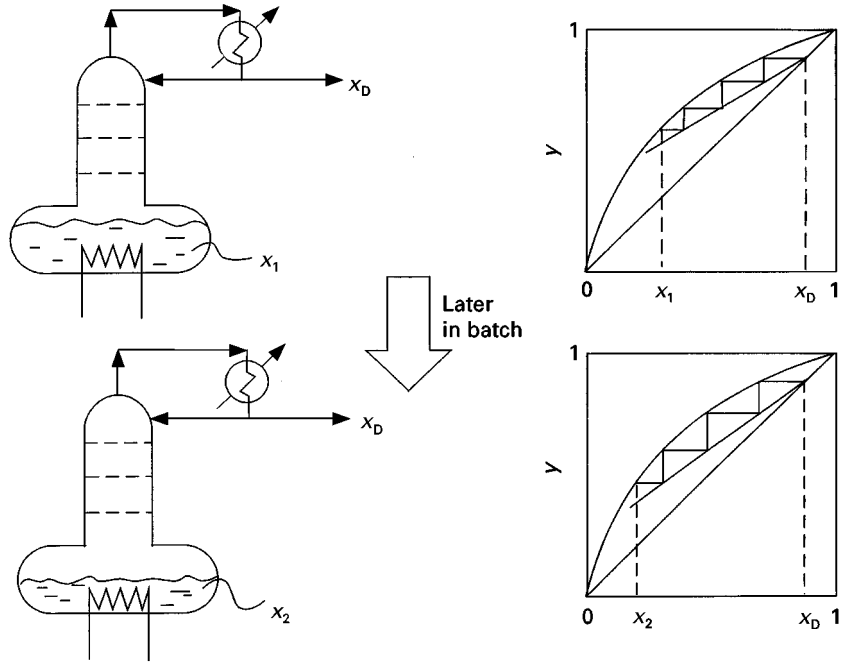


Figure 26 Reflux ratio can be varied in batch distillation to maintain overhead product purity.

pressure. The second method is to add a mass separation agent (known as an entrainer or a solvent). The mass separating agent must change the relative volatility of the original mixture in a way which allows the separation to be achieved.

Steam Stripping

Sometimes live steam is added at the base of the distillation column. When steam is used in this way, for example for the separation of hydrocarbon mixtures, the steam acts as an inert carrier, the presence of which decreases the partial pressure of the components in the vapour phase. This is like operating the distillation column at a lower pressure as far as the separation is concerned. However, the use of stripping steam is not quite the same as reducing the operating pressure.

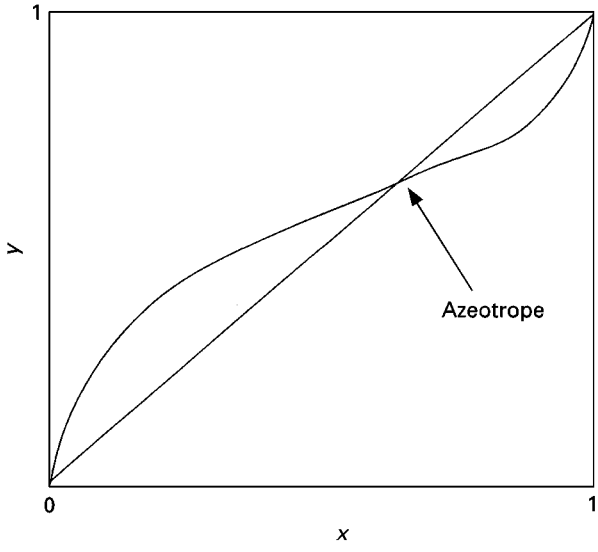


Figure 27 Azeotropic behaviour.

Intermediate Reboiling and Condensing

Rather than use a single reboiler at the bottom of the column and a single condenser at the top of the column, it is possible to add or reject heat at intermediate points within the column. Below the feed but above the base of the column, liquid can be withdrawn from one of the stages into an intermediate reboiler to be vaporized and the vapour returned to the column. This inter-reboiling substitutes part of the reboiling at the base of the column. The advantage of inter-reboiling is that the heat can be supplied at a lower temperature in the inter-reboiler, compared with the temperature required for the reboiler at the base of the column.

Similarly, vapour can be withdrawn from the column above the feed but below the top of the column, condensed and the liquid returned to the column. Cooling in the intercondenser substitutes cooling in the overhead condenser. Because the cooling in the intercondenser is carried out at a higher temperature than the overhead condenser, this can have advantages in terms of the utility costs. In practice, it is difficult to extract part of the vapour flowing up

DropBooks

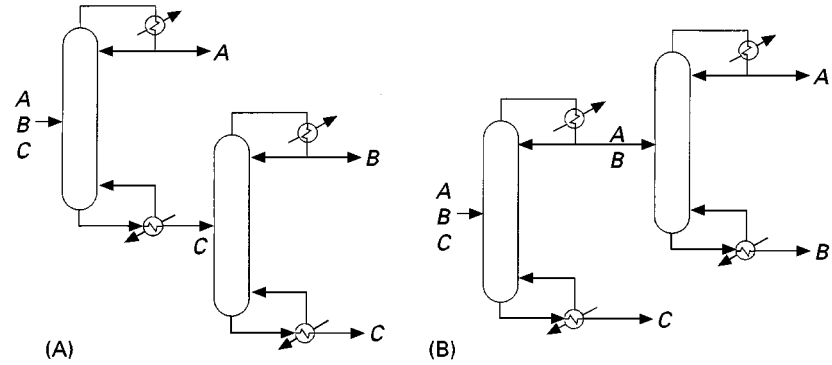


Figure 28 Sequencing simple distillation columns. (A) Direct sequence; (B) indirect sequence.

the column into an intercondenser. Because of this, it is more usual to take a liquid side-stream from the column, sub-cool the liquid and return the sub-cooled liquid to the column. The sub-cooled liquid provides condensation directly. Such arrangements are known as pump-arounds or pump-backs.

Multiple Feeds

Sometimes it is necessary to separate two or more streams with the same components but with different compositions. If this is the case, it is wrong to mix the streams with different compositions to produce a single feed for the distillation column. This is because we would mix streams only to separate them later and this is thermodynamically inefficient. If we have several streams with the same components but significantly different compositions, then it is better to feed them to the distillation column at different points, trying as much as possible to match the composition of each feed with that of one of the stages in the column.

Multiple Products

It is sometimes possible to withdraw more than two products from the same column. Part of the liquid flowing down the column or part of the vapour flowing up the column can sometimes be taken as a side-stream to form a third product. Such side-stream column designs are only possible under special circumstances.

Column Sequences

If a feed mixture needs to be separated into more than two products, then more than one distillation column will usually be required. **Figure 28** illustrates the options for the separation of a mixture of three products. In the first arrangement, the lightest component is taken overhead first and the two heavier products are separated in the second column. In the second arrangement, the heaviest product is separated first and then the two lightest products are separated in the second column. For a three-product separation, there are two possible sequences, as shown in Figure 28. As the number of products in the mixture increases, the number of possible distillation sequences increases significantly. For example, if we have six products, then there are 42 possible sequences of columns.

Thermal Coupling

Figure 28 showed different arrangements of simple distillation columns for the separation of a three-product mixture. Each column had one feed,

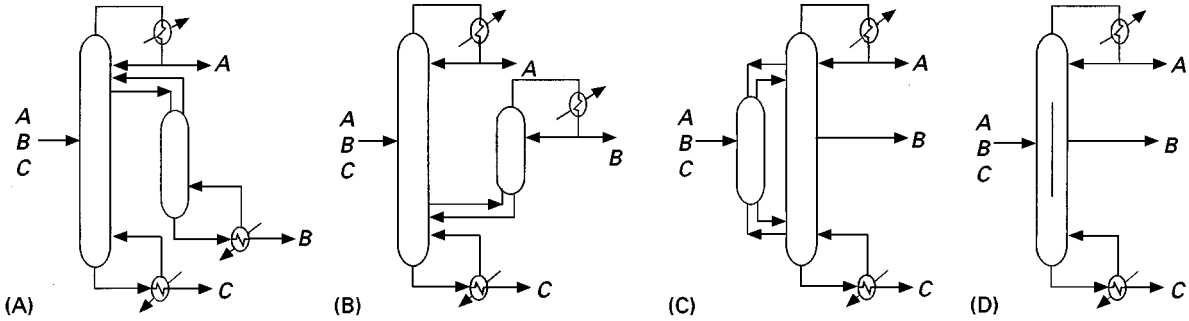


Figure 29 Thermally coupled columns. (A) Side-stripper, (B) side-rectifier; (C) fully thermally coupled (Petlyuk) column; (D) dividing wall column.

Table 1 Cases not suited to separation by distillation

Case	*Problem*	*Possible solutions*
Separate materials of low molecular mass	Low condensation temperature	Absorption, adsorption, membranes
Separate heat-sensitive materials of high molecular mass	Thermal degradation of products	Vacuum distillation
Separate components present in low concentrations	High flow rates in columns	Absorption, adsorption
Separate classes of components (e.g. aromatics from aliphatics)	Boiling temperatures/volatilities of components in a class are not adjacent	Liquid–liquid extraction
Separate components with similar relative volatilities	Difficult separation: high operating and capital costs	Add mass separating agent and employ extractive or heterogeneous distillation or liquid–liquid extraction, crystallization
Separate components which form an azeotrope	Azeotrope limits product composition	Add mass separating agent and employ extractive or heterogeneous distillation or liquid–liquid extraction, crystallization
Separate volatile and involatile components	Distillation requires that all components are mobile for countercurrent flow	Evaporation, drying, nanofiltration
Separate condensible and noncondensible components	Only partial condenser can be used overhead	Use single-stage separation (flash)

two products and had a reboiler and a condenser. Sometimes, it is desirable to exchange heat between columns directly using thermal coupling connections. **Figure 29** shows some thermally coupled distillation designs for the separation of a three product mixture. Figure 29A shows a side-stripper and Figure 29B a side-rectifier. Figure 29C shows a fully thermally coupled arrangement, sometimes known as a Petlyuk column. Figure 29D shows what is known as a dividing wall column. This is the same arrangement as the Petlyuk column but the arrangement is built in a single shell with a dividing wall down the middle of the column. The arrangements in Figure 29C and 29D are both equivalent thermodynamically, if there is no heat transfer across the dividing wall in Figure 29D.

Summary

Distillation is a versatile, robust and well-understood technique and is the most commonly used method for the separation of homogeneous fluid mixtures. There are cases for the separation of homogeneous fluid mixtures for which distillation is not well suited. **Table 1** presents a summary of these cases, along with possible solutions. It should be noted, however, that even though distillation is not well suited to the separation duties in Table 1, distillation is still used in some form for many of these problematic cases.

Symbols

b_i	bottoms flow rate of component i
B	molar bottoms flow rate
d_i	distillate flow rate of component i
D	molar distillate flow rate
E_M	Murphree tray efficiency
E_{MP}	point efficiency
E_o	overall tray efficiency
f_i^L	fugacity of component i in the liquid phase
f_i^V	standard-state fugacity of component at the temperature of the system
f_i^0	fugacity of component i in the vapour phase
F	molar feed flow rate
H	molar enthalpy
K_i	equilibrium constant for component i
L	molar flow of liquid
N_{min}	minimum number of stages
N	number of stages
N_{comp}	number of components
P	system pressure
P_i^{SAT}	saturated vapour pressure of component i at the system temperature
q	feed condition
Q	heat duty
R	reflux ratio
r	recovery
R_{min}	minimum reflux ratio
T	temperature
U	vapour velocity
V	molar flow of vapour
x_i	mole fraction of i in the liquid phase
y_i	mole fraction of i in the vapour phase
y_j^*	mole fraction of vapour that would be in equilibrium with liquid leaving stage j
$y_{j,local}^*$	mole fraction of vapour that would be in equilibrium with the local concentration on stage j
z_i	feed composition of component i
α_{ij}	relative volatility between components i and j
ρ	density
ϕ_i^L	liquid-phase fugacity coefficient for component i

DropBooks

ϕ_i^V vapour-phase fugacity coefficient for component *i*
γ_i activity coefficient for component *i*

See Colour Plate 5.

Further Reading

Geankoplis CJ (1993) *Transport Processes and Unit Operations*. New Jersey: PTR Prentice Hall.

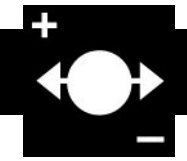
King CJ (1980) *Separation Processes*. New York: McGraw-Hill.

Kister HZ (1992) *Distillation Design*. New York: McGraw-Hill.

Seader JD and Henley EJ (1998) *Separation Process Principles*. New York: John Wiley.

Stichlmair JG and Fair JR (1998) *Distillation Principles and Practice*. New York: Wiley-VCH.

ELECTROPHORESIS



D. Perrett, St Bartholomew's and the Royal London School of Medicine and Dentistry,
St Bartholomew's Hospital, London, UK

Copyright © 2000 Academic Press

An Outline of the Historical Background to Electrophoretic Separations

The movement of charged particles under the influence of an electric field was observed as long ago as 1807 by Ferdinand Frederic Reuss. In 1909, the term, electrophoresis, was introduced by Michaelis as a description of this phenomenon and is derived from the Greek word *elektron* meaning amber (i.e. electric) and *phore* meaning bearer. Yet it was not until the 1930s that electrophoresis, as we know it today, developed from the work of Tiselius, who, in 1948, was awarded the Nobel Prize for this development. **Table 1** charts the development of the technique over the last century. By the 1950s electrophoresis was a common laboratory technique equivalent in usefulness to planar chromatography techniques such as paper and thin layer. However, with the advent of high-performance liquid chromatography (HPLC) in the 1970s, analytical electrophoresis became something of a 'Cinderella' technique. Only in biochemical and clinical laboratories did electrophoresis continue in use as a qualitative separation technique for macromolecules, such as proteins and DNA.

It has been claimed that currently at least half of all separations are performed by electrophoresis since separations of blood proteins and DNA digests are routinely performed by the technique. The technique is now so routine in biomedicine and related disciplines that it is rarely referred to in the abstracts and titles of papers where it is a core technology, for example DNA sequencing. Even so, it is mentioned by name in almost as many papers as is chromatography (**Table 2**). However, with the development of capillary electrophoresis after 1981 electrophoresis has returned as a substantial topic of interest to mainstream analytical chemistry.

Fundamentals of Electrophoresis

Unlike chromatography, there is no formal International Union of Pure and Applied Chemistry (IUPAC) definition of electrophoresis, although one is being developed at the time of writing. However, through teaching the subject over the past 10 years, I have developed the following definition:

> 'Electrophoresis is a mainly analytical method in which separations are based on the differing mobilities (i.e. speed plus direction of movement) of two or more charged analytes (ionic compounds) or particles held in a conducting medium under the influence of an applied direct current electric field' (**Figure 1**).

Electrophoresis therefore contrasts to chromatography which is defined as a method used primarily for the separation of two or more components of a mixture, in which the components are distributed between two phases, one of which is stationary while the other moves. Another difference is that in chromatography the modelling of the separation from first principles is complex, difficult and imprecise whereas a relatively simple theoretical background to electrophoresis has been developed and is reproduced below. For a more complete discussion of electrophoretic theory see Mosher *et al*. (1992).

In electrophoresis the movement is towards the electrode of opposite charge to that of the particle or ion being separated. Cations are positively charged ions and move towards the negative electrode (the cathode). Anions are negatively charged ions and move to the positive electrode (the anode). It is important to note that neutral species do not move under the influence of the electric field, although they